

Job's Method of Continuous Variation

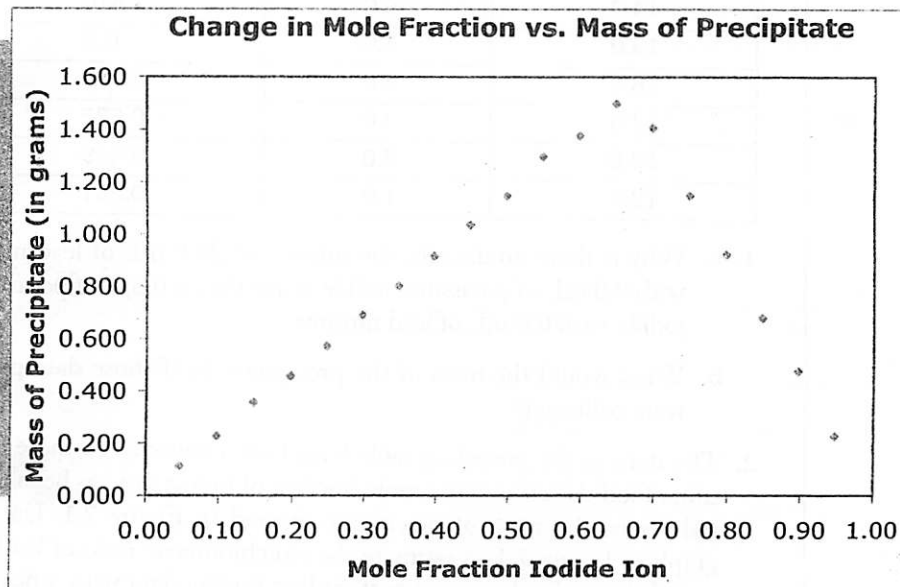
PURPOSE

- Determine the stoichiometry of a chemical reaction experimentally
- Determine the chemical formula of a precipitate
- Determine the oxidation state of an ion in solution

INTRODUCTION

How can the stoichiometry of a chemical reaction or the formula of a compound be determined experimentally? It can be done using **Job's Method of Continuous Variation**, which keeps the *total* number of moles of reactants *constant* throughout a series of mixtures of reactants, but varies the mole fraction of each reactant from mixture to mixture. Certain specific measurements are then taken for each of the mixtures. Because the maximum change will occur when the mole fraction of the reactants is closest to the actual stoichiometric mole ratio, both the formula of the product and the reactant stoichiometry can be determined using this approach. Specifically, by measuring the change in temperature, the pH, the absorbance, and the mass of precipitate formed for each reaction mixture, and by graphing these measurements versus mole fraction, one can determine the mole fraction for each reactant that produces the maximum change.

Figure 7.1
By measuring changes in various states of a solution in relation to the mole fraction of its reactants, one can find the mole fraction that produces maximum change. This graph relates mass of precipitate formed to mole fraction.



Keep in mind that the maximum change will occur when each reactant is a *limiting* reactant. So, the graph of mole fraction versus change will show a region starting when the mole fraction of this reactant is zero and increasing as the mole fraction of this reactant increases until the stoichiometric mole ratio of reactants is reached. In this region, the slope of the change will be positive, and the limiting reactant will be the reactant being graphed. When the maximum change is reached, the other reactant becomes the limiting reactant, and the magnitude of the change drops, resulting in a negative slope in this region. Where the change is biphasic, there will be a region with a positive slope for the mole-fraction range in which the reactant graphed is the limiting reactant, and a region with a negative slope for the range in which the reactant graphed is in excess. The point at which these lines intersect is the experimental value for the mole fraction of the reactant that produces maximum change when both reactants are limiting reactants. The ratio of mole fractions of ion in this compound will be used to determine the chemical formula of the product and the stoichiometric ratio. The ratio of these mole fractions is the stoichiometric ratio of the reactants in the chemical reaction. The oxidation number of the reacting ion can then also be determined.

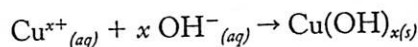
Pre-Lab Questions

A student was trying to determine the formula of a lead iodide precipitate by mixing solutions of 0.1 *M* potassium iodide with 0.1 *M* lead nitrate. The experimental data are given in this table.

Volume of 0.1 <i>M</i> potassium iodide (mL)	Volume of 0.1 <i>M</i> lead nitrate (mL)	Mass of precipitate formed (g)
1.0	19.0	0.115
2.0	18.0	0.230
3.0	17.0	0.359
4.0	16.0	0.460
5.0	15.0	0.575
6.0	14.0	0.695
7.0	13.0	0.805
8.0	12.0	0.920
9.0	11.0	1.040
10.0	10.0	1.150
11.0	9.0	1.300
12.0	8.0	1.380
13.0	7.0	1.500
14.0	6.0	1.410
15.0	5.0	1.150
16.0	4.0	0.924
17.0	3.0	0.682
18.0	2.0	0.479
19.0	1.0	0.231

1. a. Why is there no data for the mixture of 20.0 mL of lead nitrate with 0.0 mL of potassium iodide or for the 20.0 mL of potassium iodide with 0.0 mL of lead nitrate?
- b. What would the mass of the precipitate be if those data points were collected?
2. The data in the preceding table have been converted to mole fraction of iodide ion, and the mole fraction of iodide ion has been plotted versus the mass of precipitate formed in Figure 7.1. Use the graph in Figure 7.1 to estimate the stoichiometric ratio of lead ion to iodide ion by drawing a best-fit line for the data with a positive slope and a separate best-fit line for the data with a negative slope. Drop a perpendicular to the *x*-axis from the intersection point of these best-fit lines to determine the mole fraction of the iodide ion needed to form the maximum mass of precipitate.
 - a. What is the mole fraction of lead nitrate at this point?
 - b. What is the mole fraction of potassium iodide at this point?
 - c. Determine the stoichiometric ratio between these ions by taking the ratio of the mole fractions you found in questions 2a and 2b.
 - d. Write the formula for the precipitate.
 - e. Write a balanced net-ionic equation for the reaction that forms this precipitate.

Procedure Preview In the procedural methods that follow, an exothermic reaction between aqueous solutions of sodium hydroxide and a copper ion of unknown oxidation state will be investigated. Because this reaction is a precipitation reaction, you will also measure the height of the precipitate in each test tube after it settles overnight. These experimental data will not only determine the stoichiometry of the reaction, but they will also be used to determine the formula of the precipitate and the oxidation number of the copper ion:



Note: Methods 1, 2, and 3 use identical procedures to make the sample solutions, so the same samples produced during Method 1 can later be analyzed using Method 2, where the pH of each sample is measured, and then again using Method 3, where the absorbance at 635 nanometers (nm) is measured with a colorimeter. Similarly, Methods 4 and 5 use identical procedures to make sample solutions, so the samples whose temperature change is measured during Method 4 can be used to measure the mass of precipitate formed in the reaction by filtration in Method 5.

Method 1: Height of Precipitate and Qualitative Observations

In this experiment, you will mix known volumes of sodium hydroxide solution with known volumes of a copper ion solution, keeping the total volumes of solutions mixed to 10.00 mL. After thoroughly mixing the reactants and allowing the precipitate to settle overnight, you will take careful observations of the solid and the solution and measure the height of the precipitate. By graphing the mole fraction of hydroxide ion versus the height of the precipitate, you will be able to determine the ratio of mole fractions of the reactants ($\chi_{\text{copper ion}}$ and $\chi_{\text{OH}^{-}}$). The ratio of these mole fractions ($\chi_{\text{copper ion}}/\chi_{\text{OH}^{-}}$) can be used to determine the stoichiometric ratio of the reactants and then the formula of the hydroxide product and the oxidation state of the copper ion.

MATERIALS

- two 50-mL burets (or two 10.00-mL graduated pipets)
- standardized 1 M sodium hydroxide solution
- copper sulfate solution of same molarity
- test tubes and test tube rack
- stirring rods
- ruler

PROCEDURE

Step A Label thirteen test tubes sequentially from 1 through 13. Use a clean and rinsed buret (or graduated pipet) to deliver the volume of copper ion solution to each test tube. Record the exact volume added in your data table. Repeat the following steps for each of the 13 test tubes.

Step B Using a clean and rinsed buret (or graduated pipet), deliver the appropriate volume of standardized hydroxide solution to the test tube, being careful not to contaminate the buret (or pipet tip). Record the exact volume of hydroxide solution added.

PROCEDURE
(continued)

Test Tube #	Volume copper ion (mL)	Volume OH ⁻ (mL)
1	0.00	10.00
2	1.00	9.00
3	2.00	8.00
4	2.50	7.50
5	3.00	7.00
6	3.33	6.67
7	4.00	6.00
8	5.00	5.00
9	6.00	4.00
10	7.00	3.00
11	8.00	2.00
12	9.00	1.00
13	10.00	0.00

Step C Stir the mixture carefully with a stirring rod and then cover the test tube with a rubber stopper.

Step D Let the precipitate settle for a period of time, as directed by your teacher.

Step E Remove the test tube from the rack and rest its bottom on the lab bench. Hold the test tube straight upright.

Step F Measure the height of the precipitate. Repeat for each sample.

Step G Arrange the test tubes side-by-side in the rack in order of increasing volume of hydroxide added. Placing a sheet of white paper behind your samples, carefully observe both the precipitate and the **supernatant**—that is, the solution on top of the solid. Record these observations in your data table.

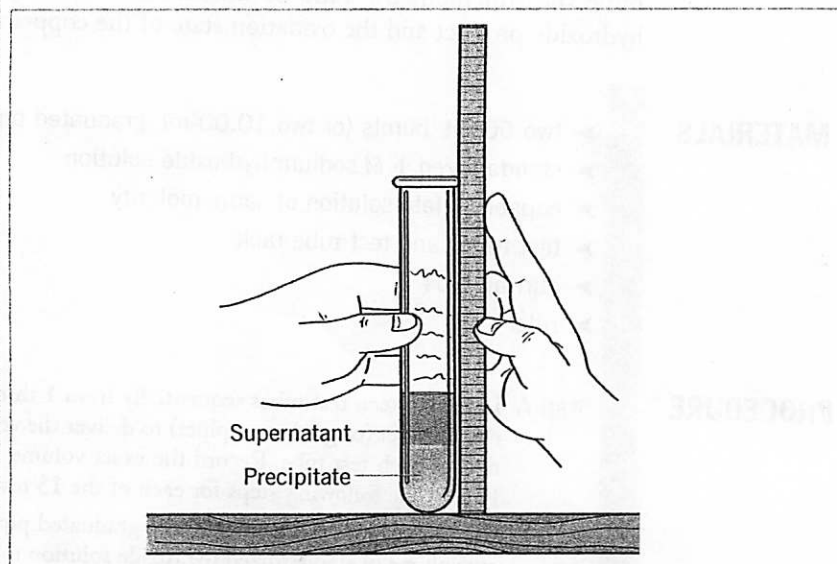


Figure 7.2 Be sure to allow sufficient time for the precipitate to settle out before measuring and recording.

PROCEDURE (continued)

Calculations (Method 1)

1. Present all your data in tabular form.
2. Calculate the mole fraction of both the copper ion and the hydroxide ion in each sample.
3. Using your observations, list the test tubes in which the copper ion is the reactant in excess.
4. Using your answers to calculations 1–3, predict the stoichiometric ratio of the chemical reaction.
5. Graph the mole fraction of copper ion versus the height of precipitate. Draw a line of best fit for both the positive and negative slope regions. Drop a perpendicular from the intersection point to the x -axis to find the mole fraction of the copper ion that produces maximum change.
6. Use your answer to calculation 5 to determine the mole fraction of hydroxide ion at the intersection point. Use these mole fractions to determine the formula of the ionic compound that precipitated in the reaction.
7. Determine the stoichiometric ratio of copper ion to hydroxide ion for this reaction.
8. Write a balanced net-ionic reaction equation for the precipitation reaction.

Method 2: pH

This method uses the same procedure for steps A–D as in Method 1, so the samples sealed in the test tubes after data collection in Method 1 may be used.

Step E Follow your teacher's directions to standardize your pH probe.

Step F Without disturbing the precipitate, carefully place the pH probe in the test tube so the glass bulb on the bottom is covered by the solution.

Step G Allow the pH reading to become constant. Then record the pH reading in the data table.

Step H Repeat for each sample.

Calculations (Method 2)

1. Present all of your data in tabular form.
2. Calculate the mole fraction of both the copper ion and the hydroxide ion in each sample.
3. Graph mole fraction of copper ion versus pH.
4. The graph you made for calculation 3 is called a **titration curve**. Follow the instructions outlined in Experiment 10, Method 3, on page(s) 71–79 to determine the equivalence point on the titration curve. Your instructor will tell you which specific approach outlined there to follow to determine the equivalence point on your titration curve graph.
5. Using your answers from calculation 4, calculate the mole fraction of hydroxide ion at that point. Then use the ratio of mole fractions of copper ion to hydroxide ion to determine the formula of the ionic compound that precipitated in the reaction.
6. Determine the stoichiometric ratio of copper ion to hydroxide ion for this reaction.
7. Write a balanced net-ionic reaction equation for the precipitation reaction.

Method 3: Absorbance at 635 Nanometers

This method uses the same procedure for steps A–D as in Method 1, so the samples sealed in the test tubes after data collection in Method 1 can be used.

Step E Be sure your spectrophotometer is warmed up. Follow the teacher's directions to zero your colorimeter (or Spectronic 20) at 635 nm.

Step F Without disturbing the precipitate, carefully remove a sample from the test tube, using a transfer pipet, and place in cuvette. Be sure to fill the cuvette with the appropriate volume of sample. (Ask your teacher what to do if you do not have sufficient sample to fill the cuvette. You will be told how to perform a careful dilution using distilled water and how to correct the measured absorbance for any dilution.)

Step G Be sure no solid is in the sample, then remove all air bubbles. Wipe the outside of cuvette with a damp paper towel to remove any fingerprints or dirt.

Step H Place the cuvette in the colorimeter (or Spectronic 20) and close the cover. Read absorbance at 635 nm and record in data table.

Step I Repeat for each sample.

PROCEDURE (continued)

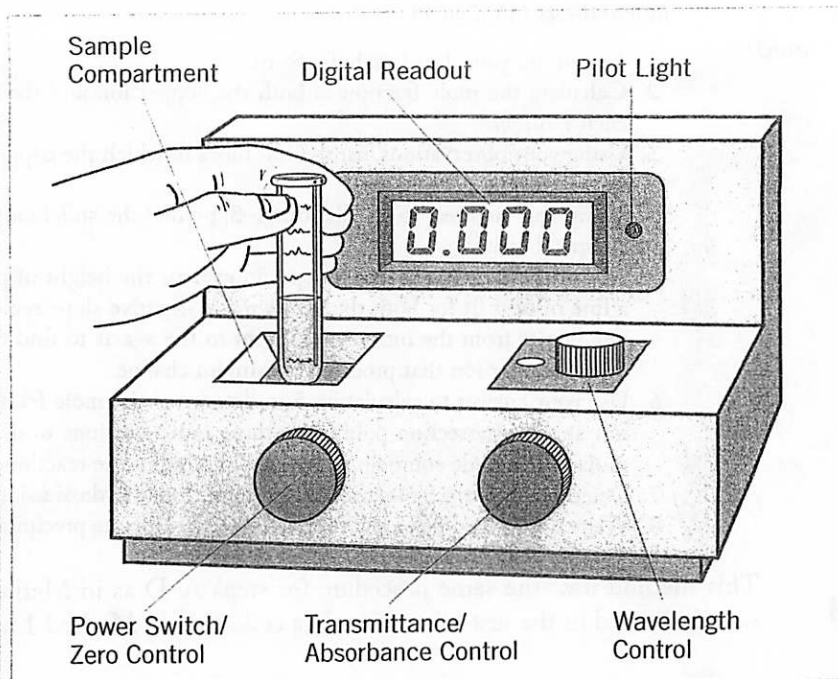


Figure 7.3

Calculations (Method 3)

1. Present all of your data in tabular form.
2. Calculate the mole fraction of both the copper ion and the hydroxide ion in each sample.
3. Graph mole fraction of copper ion versus absorbance.
4. Carefully analyze this graph to determine the mole fraction of copper ion when there is a significant change in the absorbance readings.
5. Using your answer to calculation 4, calculate the mole fraction of hydroxide ion at that point, and then use the ratio of mole fractions of copper ion to hydroxide ion to determine the formula of the ionic compound that precipitated in the reaction.
6. Determine the stoichiometric ratio of copper ion to hydroxide ion for this reaction.
7. Write a balanced net-ionic reaction equation for the precipitation reaction.

Post-Lab Questions

1. Can the stoichiometric ratio be determined by the colors of the resulting supernatants? Explain.
2. Could the oxidation state of the copper ion be determined by looking at the solution? Explain.
3. Would any of these methods work to determine the reaction stoichiometry for a reaction between the hydroxide ion and the zinc ion? If yes, which methods could you use and why would they work?
4. Could the graphs use the mole fraction of hydroxide ion instead of the mole fraction of copper ion to determine the reaction stoichiometry? If no, explain why not. If yes, explain how the shape of the graphs would change.